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R.H. SAUNDERS GS - BEDROCK STUDY
GEOCHEMICAL INVESTIGATIONS

Report No 88-323-K

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Abstract

In this report, we have presented a brief review of pertinent literature on gypsum dissolution, with particular reference to the relevant geochemical approaches employed to evaluate void formation and enlargement in the foundation rock. A geochemical evaluation of the existing water chemistry data from the R.H. Saunders GS site is also presented.

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R.H. SAUDERS GS - BEDROCK STUDY
GEOCHEMICAL INVESTIGATION

1.0 INTRODUCTION

The dissolution of gypsum and anhydrite is known to cause serious problems in engineering structures in that it can result in the formation and subsequent enlargement of fissures and caverns leading to excessive settlement or subsidence. Many dams and reservoirs have performed inadequately because of the presence of gypsiferous rock in their foundations or abutments (James and Lupton, 1978).

During the 1987 Dam Safety Investigations at R.H. Saunders GS (Grass, 1987), an open cavernous feature was encountered in borehole SM-6 at a depth of 190 ft below the tunnel level. Subsequent field investigations at the site conducted jointly by the Civil Research Department and the Geotechnical and Hydraulic Engineering Department in 1988 established the spatial extent of the water-bearing open feature in borehole SM-6. Within the void zone in SM-6, flow measurements revealed a maximum flow velocity of 0.3 ft/s (R. Koopmans, pers. comm.). A solid gypsum bed was intercepted in borehole 88-1 (marker bed 8), 110 ft downstream from borehole SM-6. Stratigraphically, this bed is believed to correspond to the same rock horizon with the open feature in SM-6 (J. Grass, pers. comm.). A somewhat smaller open feature was also encountered at a shallower depth in borehole 88-1.

Although these open features, because of their limited spatial extent and localized nature, are not of immediate concern with respect to the overall structural stability of the dam, it is important to consider the effect of the high artesian flow observed in SM-6 and 88-1. Also, it is important to take note of the reducing character of the water at depth in these boreholes, on gypsum dissolution and possible subsequent enlargement of existing solution voids in the foundation rock.

This report presents a brief review of the pertinent literature on gypsum dissolution, paying particular attention to the basic parameters controlling gypsum dissolution and to the relevant geochemical approaches employed to evaluate the stability of dams on gypsiferous rock foundations.

This is followed by a geochemical evaluation of existing water chemistry data from the R.H. Saunders GS site. Finally, a tentative outline of work proposed for 1989 is presented.

2.0 REVIEW OF RELEVANT LITERATURE

Dissolution of gypsum has been a subject of many investigations and, as a result, various rate equations have been proposed for the dissolution phenomena (Barton and Wilde, 1971; Liu and Nancollas, 1971; James and Lupton, 1978; Karen and Shainberg, 1981; Gobran and Miyamoto, 1985). It is generally recognized, however, that gypsum dissolution is controlled primarily by the surface area in contact with the water, the flow velocity of water past a unit area of gypsum, and the groundwater chemistry.

James and Lupton (1978) proposed the following rate equation for gypsum dissolution

$$dM/dt = KA\ (C_s - C) \qquad (1)$$

where M = mass of gypsum dissolved at time t

C_s = equilibrium concentration

C = dissolved gypsum in solution at time t

A = surface area of gypsum exposed to water

K = dissolution rate constant

The surface area, A, for the system under study has to be estimated, based on field observations. The dissolution rate constant, K, is normally determined experimentally and there is no consensus on reaction order (Gobran and Miyamoto, 1985). The term (C_s-C) is a measure of the degree of undersaturation of the groundwater, relative to gypsum solubility. The equilibrium concentration, C_s, which varies with solution chemistry, temperature, and pressure, can be defined using available geochemical computer programs such as PHREEQE.

James and Lupton developed a method to estimate quantitatively the rate and extent of the dissolution of gypsum in foundation rock. There are basically three important factors to be considered: (a) the occurrence and distribution of gypsum in the foundation rock; (b) establishment of the flow regime and velocities associated with the gypsum beds and other permeable strata; and (c) definition of the occurrence and dimensions of fissures in gypsum beds.

Based on the above information, James and Lupton were able to estimate the rate of void enlargement at a given site, as well as predict potential instability problems with the rock mass and the dam. They identified the following situations as potentially dangerous with respect to stability of the foundation rock: (a) presence of gypsum as a cementing agent in a relatively

strong conglomerate; (b) existence of massive anhydrite beds in the foundation rock; and (c) the size of fissures in massive gypsum (larger than 0.3 mm in width).

A somewhat different approach was taken by Claassen (1981). In Claassen's method, an estimate was made of the chemical composition of water recharging the system and the difference between that estimate and the composition of groundwater in the system was used to determine the minimum amount of calcium sulfate being dissolved under existing hydrologic conditions. This result was used, with published data on rates of calcium sulfate dissolution, to estimate the effective surface area involved in the solution processes. Finally, the rate at which solution openings are growing can be estimated.

3.0 EVALUATION OF AVAILABLE GEOCHEMICAL DATA

The chemical data for water samples taken from shallow pressure relief wells and deep observation wells during the past 18 years (1970 - present) was provided by A.R. Bennett of the Civil Works Department.

The mean sulfate concentration for each well, averaged over a period of 18 years, is displayed in Figure 3.1. In qualitative terms, the data exhibit a distinct trend of significantly higher sulphate concentrations (>1500 mg/l) in deep observation wells than those observed in shallow pressure relief wells. The elevated levels of sulphate in the deep observation wells are believed to be derived from the main gypsum layer (marker bed #7) which is intercepted by these wells. In contrast, no such gypsum layer is encountered in the shallow pressure relief wells.

However, the water chemistry data gathered at the R.H. Saunders GS site during the past 18 years are incomplete and, therefore, not amenable to geochemical modeling for evaluation of gypsum dissolution in the foundation rock at the site.

One water sample, taken recently from borehole SM-6 has been analyzed for all major components (Table 3.1), and the analytical data has been used to define its geochemical character. It is found that this particular sample is saturated with respect to gypsum (Table 3.2). At the time of sampling, the water sample imparted a strong H_2S odour, indicating strongly reducing conditions. However, by the time the sample was analyzed, all the H_2S had escaped and the sulphide had oxidized to sulphate. This is also evident from the below detection levels of dissolved sulphide (Table 3.1).

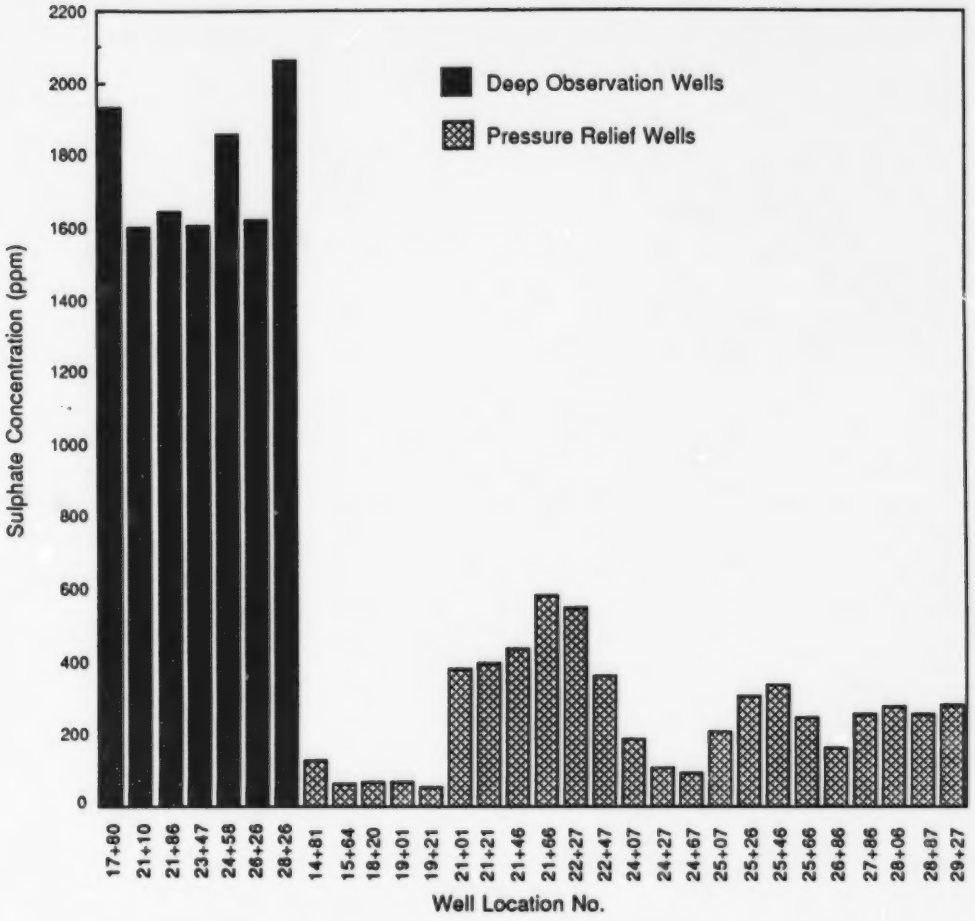

Fig. 3.1. Sulphate concentrations in water samples from deep observation and shallow pressure relief wells.

TABLE 3.1

CHEMICAL COMPOSITION OF SM-6 WATER SAMPLE

Components	Concentrations (ppm)
Ca^{2+}	500
Mg^{2+}	115
K^{+}	15.7
Na^{+}	232
Sr^{2+}	10
SiO_2	14.6
SO_4^{2-}	1800
Cl^{-}	174
DIC[a]	21
DOC[b]	<0.5
H_2S	<0.02

[a] Dissolved inorganic carbon

[b] Dissolved organic carbon

Oxidation of the sample not only increased the SO_4^{2-} concentration of the solution but also changed the redox condition of the system. Both effects result in an increase in the degree of saturation, relative to gypsum. Nevertheless, the solution is still found to be close to gypsum saturation even though we assumed the SO_4^{2-} concentration to be half of the reported value (Table 3.2). For subsequent water sampling, appropriate precautions will have to be taken to prevent oxidation of the water samples.

PHREEQE can compute the gypsum solubility dependence on temperature, gas pressure (eg. PCO_2), and solution chemistry. As an example, we show here the solubility dependence on the sodium chloride concentration of a solution. It was reported that the rate of dissolution of gypsum and anhydrite increase with increasing concentration of sodium chloride in solution (James and Lupton, 1978). The effect of sodium chloride concentration in groundwater on gypsum and anhydrite solubility was modeled by PHREEQE. The modeling was performed using two different approaches.

First, the saturation indices of gypsum and anhydrite were calculated for varying salt contents of solution. The Ca^{2+} and SO_4^{2-} concentrations of these solutions are assumed to be the same ($[Ca^{2+}] = SO_4^{2-} = 1.0$ mM), while sodium chloride concentration varies from 0.00M to 0.51M. The range of sodium chloride concentration selected is the same as that reported in the experimental work of James and Lupton. However, their highest NaCl concentration is not realistic and the submodels used in PHREEQE cannot be applied to solutions of very high ionic strength. The results of our model calculations are shown in Table 3.3. Even though the Ca^{2+} and SO_4^{2-} concentrations are the same in fresh water and NaCl solution, the saturation indices of gypsum and anhydrite decrease with increasing concentration of NaCl in solution (Figure 3.2). This means that the degree of undersaturation (Cs-C) will become greater, as the salt content increases. Thus, the dissolution rate of gypsum and anhydrite will increase according to equation (1).

In the second simulation, we directly compute the solubility of gypsum and anhydrite in solutions with varying concentrations of NaCl (Table 3.4). The results show that the solubilities of gypsum and anhydrite increase two-fold from fresh water to 0.71M NaCl solution (Figure 3.3). In the case of gypsum and anhydrite, the solubility is equal to the equilibrium concentration, Cs, in equation (1). Therefore, the Cs value in equation (1) will increase with increasing salt content, with a corresponding increase in the degree of undersaturation and, hence, the dissolution rate. Similarly, the effect of other ion species can also be calculated and predicted.

TABLE 3.2

SATURATION STATES OF GYPSUM AND ANHYDRITE IN SM-6 WATER SAMPLE

		Log (IAP/KT)[2]	
Mineral	Log (KT)[1]	X	Y
Gypsum	-4.61	0.17	-0.16
Anhydrite	-4.28	0.08	-0.41

[1]Log (KT) is log of equilibrium constant, K, at 25°C;

[2]Log (IAP/KT) is saturation index. A positive value means oversaturation, a negative value means undersaturation; Y has half of SO_4^{2-} content of X (observed value).

TABLE 3.3

EFFECT OF SODIUM CHLORIDE CONCENTRATION
ON SATURATION INDEX OF GYPSUM AND ANHYDRITE

NaCl Concentration (g/l)	Saturation Index of Gypsum	Saturation Index of Anhydrite
0	-1.6276	-1.9535
1	-1.8928	-2.2182
3	-2.1372	-2.4616
10	-2.5373	-2.8584
30	-3.0343	-3.3447

TABLE 3.4

EFFECT OF SODIUM CHLORIDE CONCENTRATION
ON THE SOLUBILITY OF GYPSUM AND ANHYDRITE

NaCl Conc. (M)	Gypsum (M)	Anhydrite (M)
0.0000	0.0101	0.0169
0.0171	0.0116	0.0188
0.0513	0.0134	0.0219
0.1711	0.0202	0.0302

This simple example illustrates clearly that geochemical modeling can be used quite effectively for the gypsum dissolution problem, in particular, the definition of the geochemical character of ambient groundwater relative to gypsum dissolution; calculation of the dependence of solubility, degree of undersaturation and dissolution rate on solution chemistry; and simulation of incremental changes in solution chemistry induced as a result of gypsum dissolution. All these geochemical factors and conditions are directly relevant to evaluation of the formation and subsequent enlargement of fissures and caverns in gypsiferous foundation rock which, in turn, can contribute to the overall instability of a hydraulic dam.

As discussed above, in situ flow measurements made recently in borehole SM-6 reveal a complex water flow regime (R. Koopmans, pers. comm.). The maximum flow velocity observed in the void zone in SM-6 was 0.3 ft/s. This corresponds to a relatively low dissolution rate for gypsum, relative to the range of experimental flow velocities in the James and Lupton (1978) dissolution tests (Figure 3.4).

However, it should be realized that the experimental flow velocities considered in gypsum dissolution experiments are unrealistically high. In fact, a quick calculation of groundwater velocity in karst limestone (hydraulic conductivity = 0.01 m/s), assuming a high hydraulic gradient (dh/dl = 10), yields a value which is extremely close to the flow velocity measured by R. Koopmans in SM-6 (shaded area, Figure 3.4). Therefore, considering the unrealistically high flow rates employed in the laboratory dissolution tests and the conservatively high groundwater velocity calculated for karst limestone, we conclude that the gypsum dissolution rate constant of $\sim 1.0 \times 10^{5}$ m/s, corresponding to the measured flow velocity of 0.3 ft/s, is believed to be quite high in the void zone in SM-6. It should be pointed out though that the flow velocity considered here is the maximum value observed at the site and, at the same time, represents a discrete data point in time and space.

More data on temporal and spatial variations in groundwater flow regimes and velocities are needed to obtain representative flow data for geochemical evaluation of water chemistry, relative to gypsum dissolution in the foundation rock.

Thin-section microscopic examination of two rock core samples from SM-6 (194 ft) and 88-1 (160 ft) reveals the presence of distinctive dissolution features at the periphery and along the cleavage planes of gypsum crystals (Figure 3.5). However, the dissolution voids and fissures appear to be filled in with dark, opaque material. Although preliminary at this stage, it appears that the infilling material is organic matter. More work is needed in this area to establish the presence and nature of the dissolution features, on a microscopic scale, and their effect on water flow and enhanced gypsum dissolution.

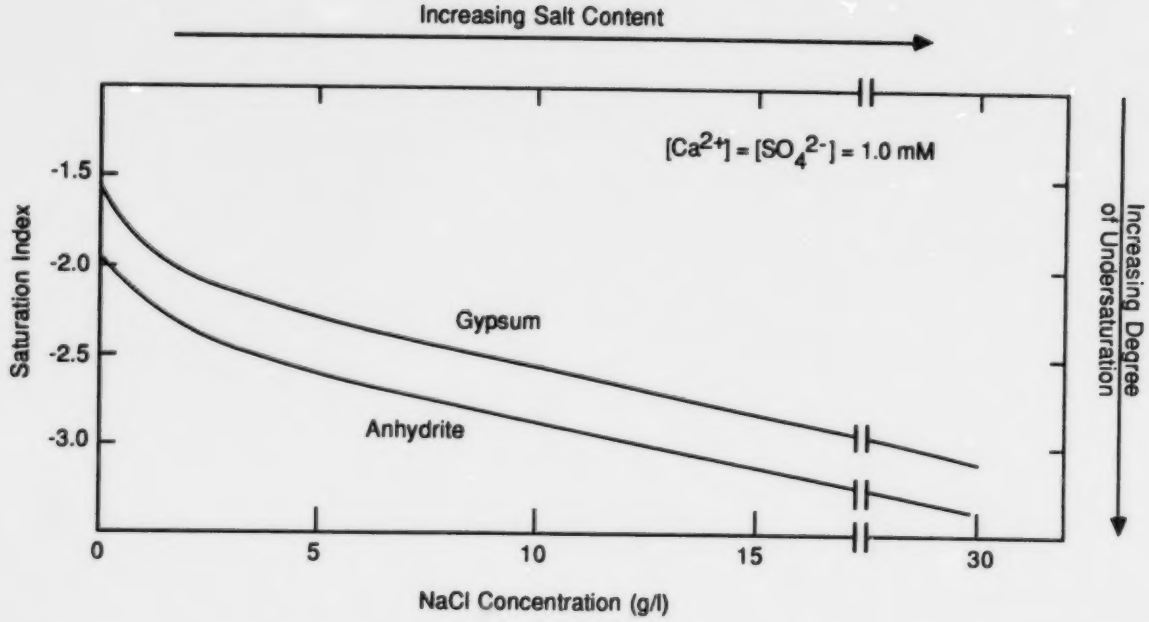

Fig 3.2. Effect of salt content of solution on the degree of saturation, relative to gypsum and anhydrite.

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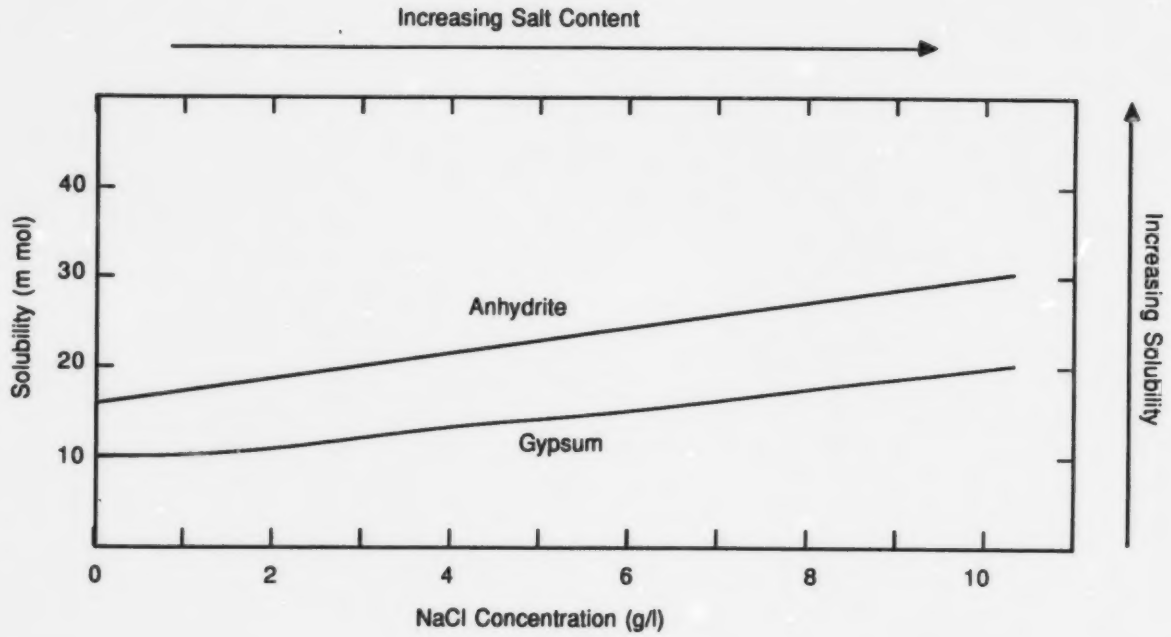

Fig. 3.3. Effect of salt content of solution on the solubilities of gypsum and anhydrite.

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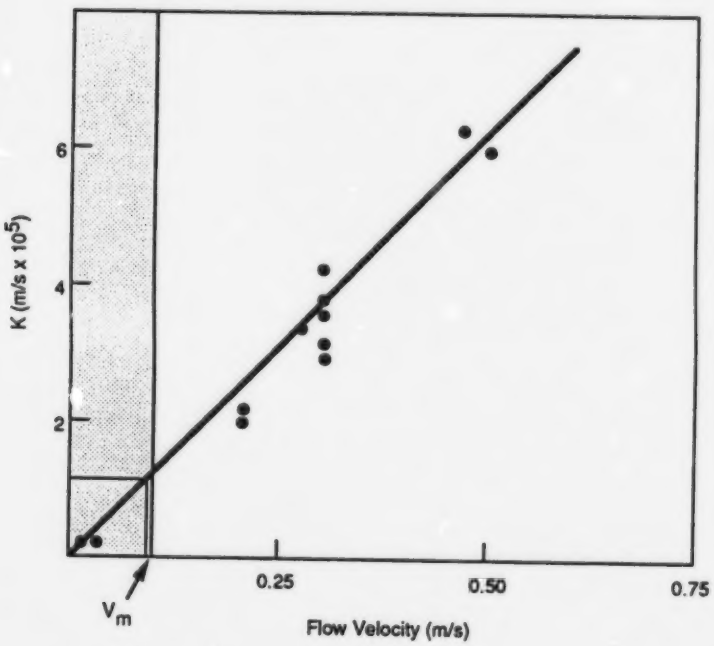

Fig. 3.4 Effect of flow velocity on the rate of gypsum dissolution (after James and Lupton, 1978). Shaded area represents the range of flow velocities in karst limestone. V_m represents the maximum flow velocity measured in the void in SM-6.

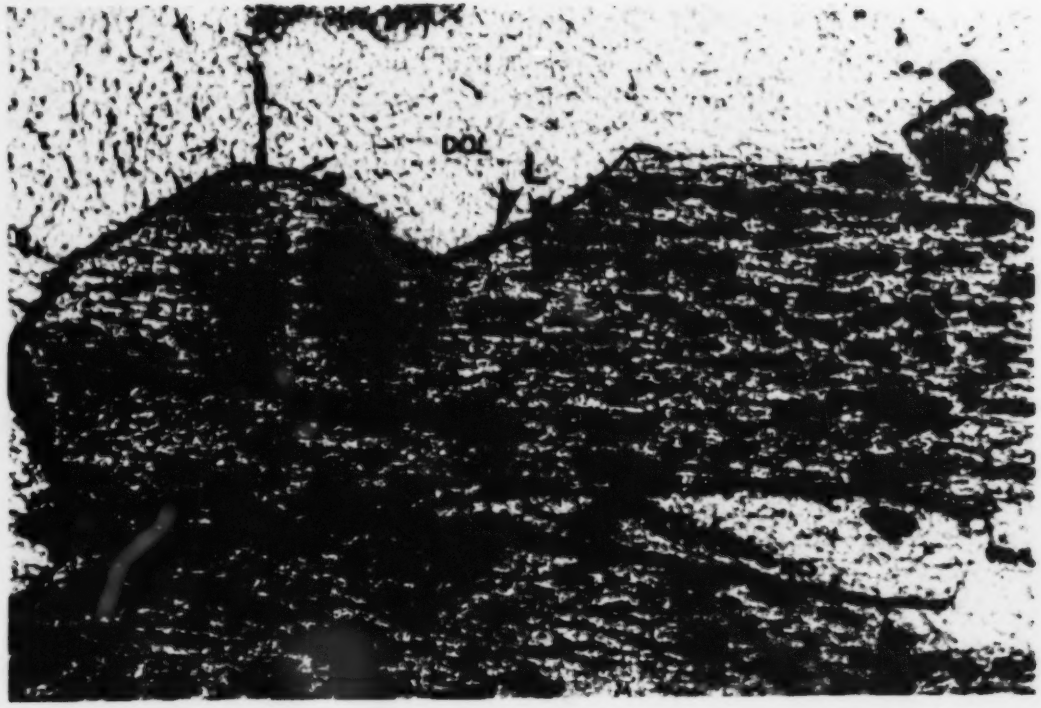

Figure 3.5

A photomicrograph of a gypsum crystal in dolomitic limestone, showing distinct dissolution features around its periphery and parallel to the cleavage planes. The dissolution pits and voids are filled in with black organic matter (ppl, 160x; DOL - dolomite; GYP - gypsum; L - dissolution features).

4.0 FUTURE WORK AND RECOMMENDATIONS

Based on the review of pertinent literature and evaluation of limited geochemical data from the R.H. Saunders GS site, it becomes apparent that the following parameters and conditions have to be established and defined in order to quantify the nature and degree of gypsum dissolution in the foundation rock below the R.H. Saunders GS dam:

(a) Distribution and occurrence of gypsum (or anhydrite) beds.

(b) Distribution, nature, and scale of dissolution features in gypsum beds.

(c) Groundwater flow regime, velocities and geochemistry of recharge and discharge waters.

(d) Laboratory kinetic data on gypsum dissolution.

Based on extensive drilling activities, sufficient information is available on item (a). At present, little information is available on the distribution, nature, and scale of dissolution features in gypsum beds. More work is definitely needed in this area.

The geochemistry of recharge and discharge waters needs to be defined. An important requirement for this study is to establish the groundwater flow pattern around the dam. An approximation of recharge water can be made if one assumed headpond river water as recharge water. For modeling purposes, the groundwater in the voids or water-bearing open features can be assumed to represent the composition of discharge waters. The groundwater flow regime and velocities at the site need to be established in detail. This information is needed in order to interpret geochemical data with respect to gypsum dissolution.

The kinetics of gypsum dissolution is not well-defined and there is no consensus on reaction order (Gobran and Miyamoto, 1985). There is a need for laboratory dissolution tests in order to define the dissolution rate of gypsum under realistic field conditions.

At part of the R.H. Saunders GS Bedrock Study - Geochemical Investigations, we propose the following work for 1989.

(a) Water Sampling and Analysis:

With the cooperation of the Civil Works Department and the Geotechnical and Hydraulic Engineering Department, water samples will be taken from selected shallow pressure relief wells and deep observation wells, employing appropriate procedures to prevent oxidation of water samples. This is important because water samples taken at SM-6 and several shallow pressure relief wells exhibit reducing properties (A. Bennett, pers. comm.) and the

redox state (SO_4^{2-} /S^{2-}) affects the saturation state of a water sample with respect to gypsum and anhydrite. In situ measurements of pH, Eh, temperature, dissolved oxygen, and conductivity will be made at the site using a specially-designed flow cell.

Following the sampling of water from selected wells under inert conditions, the water samples will be analyzed in our Analytical Services Laboratory for the major dissolved constituents. This information is needed to evaluate the degree of undersaturation of groundwater, relative to gypsum solubility.

(b) Investigation of Fissures and Dissolution Features in Gypsum Rock Cores

Samples will be extracted from selected gypsum beds for optical and scanning electron microscopy to establish the distribution, nature, and scale of dissolution fissures in gypsum beds, on a microscopic scale. This information is required to help interpret the water chemistry data in terms of gypsum dissolution and its susceptibility to chemical attack.

(c) Laboratory Determination of Gypsum Dissolution Kinetics

The rate of gypsum dissolution will be determined on selected material from R.H. Saunders GS rock cores using deionized water and headpond river water. Two types of leaching cells will be used:

(i) A leachant recirculating cell designed to achieve steady-state equilibrium conditions in a short time;

(ii) A dynamic flow-through cell designed to derive kinetic data on gypsum dissolution, as well as to study the evolving water chemistry and dissolution features with time. Specifically, two types of percolation tests will be performed: (1) crushed materials will be used in percolation tests to simulate gypsum dissolution in a porous medium; (2) In the second set, a well-characterized, massive gypsum core with a natural or an induced fracture will be tested. The leachant will be allowed to flow through the fracture at a given flow rate and the effluent chemistry monitored with time. This test will allow a correlation between the rate of fissure widening and the dissolution time, which is of direct relevance to the prediction of void solution behaviour and estimation of void enlargement in the foundation rock under field conditions and time scales.

(d) Definition of the Groundwater Flow Regime and Rates in the Foundation Rock

Since information on groundwater flow regime and velocities in the foundation rock is required to interpret geochemical data, there is a definite need for data on rates and patterns of groundwater movement through or adjacent to the gypsum layer. It is anticipated that the Geotechnical and Hydraulic Engineering Department will initiate hydrogeologic investigations at the site and generate a relevant data base.

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5.0 REFERENCES

Claassen, H.C., 1981. Estimation of calcium sulfate solution rate and effective aquifer surface area in a ground-water system near Carlsbad, New Mexico. Ground Water, 19, pp287-297.

Grass, J.D., 1987. St. Lawrence River R.H. Saunders GS design review assessment of bedrock foundation conditions. Geotechnical and Hydraulic Engineering Department Report No. 87477.

Gobran, G.R. and S. Miyamoto, 1985. Dissolution rate of gypsum in aqueous salt solutions. Soil Sciences, 140, pp. 89-93.

James, A.N. and A.R.R. Lupton, 1978. Gypsum and anhydrite in foundations of hydraulic structures. Geotechnique, 28, pp. 249-272.

Keren, R. and I. Shainberg, 1981. Effect of dissolution rate on the efficiency of industrial and mined gypsum in improving infiltration of a sodic soil. Journal of Soil Science Society of America, 45, pp. 103-107.

Liu, S.T. and G.H. Nancollas, 1971. The kinetics of dissolution of calcium sulphate dehydrate. Journal of Inorganic and Nuclear Chemistry, 33, pp. 2311-2316.